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Dielectric and Magnetic Relaxations in $\text{BaO} \cdot 2\text{TiO} \cdot 2\text{FeO}$ and $\text{BaO} \cdot 2\text{SnO} \cdot 2\text{FeO}$ (Commemoration Issue Dedicated to Professor Naokazu Koizumi on the Occasion of his Retirement)

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Dielectric and Magnetic Relaxations in $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ and $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$

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Dielectric and magnetic properties of $\text{BaO} \cdot 2\text{Ti}_{1-x}\text{Sn}_x\text{O}_2 \cdot 2\text{Fe}_2\text{O}_3$ ($0 \leq x \leq 1$) sintered samples were examined from 4.2 K to room temperature. The samples with $x < 1$ have large dielectric constant, while the sample with $x = 1$ has very small dielectric constant. Two kinds of dielectric relaxations were seen in this series of samples. The relaxation at lower temperatures (30–100 K) were found only in the samples prepared in oxygen. This relaxation seems to be caused by electron transfer between iron ions with different valence. The other dielectric relaxation observed at room temperature seems to be caused by the Maxwell-Wagner interfacial polarization. Two magnetic relaxations were found at 80 K and 165 K which are dependent on x .

KEY WORDS: Dielectric Relaxations / Magnetic Relaxation / Ferrite and Spin Glass/

1. INTRODUCTION

The existence of the phase R: $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ and $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ has been known but the physical properties of the substance R have not been known yet^{1),2)}. The substance R is composed of RR* block in $\text{BaFe}_{12}\text{O}_{19}$.³⁾ $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ can be mixed with $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ in all range of composition as solid solution. Although the substance R shows spin glass behavior, its origin is not clear⁴⁾. The spin glass behavior disappears with increasing Sn concentration in the formula $\text{BaO} \cdot 2\text{Ti}_{1-x}\text{Sn}_x\text{O}_2 \cdot 2\text{Fe}_2\text{O}_3$. It is interesting to investigate the difference in ionic and electronic structure between $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ and $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ which have the same crystal structure. In this work dielectric and magnetic measurements as well as x-ray diffraction were carried out for these series of samples. We found large difference in dielectric constant and conductivity between these two substances. Two kinds of dielectric relaxations were confirmed and their origins are considered. Two magnetic relaxations found below 165 K are studied in connection with the spin glass transition.

2. EXPERIMENTAL

The samples were prepared by calcining the mixture of BaCO_3 , TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ at 1250°C either in air or oxygen. The samples were confirmed to be composed of one phase by x-ray diffraction method. We prepared samples containing different amount of TiO_2 and Fe_2O_3 as shown in Table I. The substances R1 and R2 contain small amount of second phase which does not affect the physical properties of R. The sample with

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Table I Composition of samples in mol %

Compound	BaO	TiO ₂	Fe ₂ O ₃
R and R'	20	40	40
R1 and R1'	20	42.5	37.5
R2	20	45	35

Table II Lattice constant of samples

Sample	a/A	c/A
BaO • 2TiO ₂ • 2Fe ₂ O ₃	5.843	13.611
BaO • 2SnO ₂ • 2Fe ₂ O ₃	5.965	13.765

various Sn concentration ($x=0, .3, .6, 1.0$ in the formula $\text{BaO} \cdot 2\text{Ti}_{1-x}\text{Sn}_x\text{O}_2 \cdot 2\text{Fe}_2\text{O}_3$) were prepared. These samples are of single phase and lattice constant becomes large with increasing Sn concentration. The comparison of lattice constant between $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ and $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ is given in Table II. The samples have disk shape of 25 mm diameter and 4 mm thick. Dielectric measurements were carried out by a YHP Model 4274A LCR meter and an Ando Electric TRIC transformer bridge.

3. RESULTS AND DISCUSSION

The dielectric constant of R is about 30 at 4.2 K and increases rapidly with increasing temperature as shown in Fig. 1. Figure 2 represents dielectric constants at room temperature in the frequency range from 0.1 to 100 kHz. Large dielectric constant

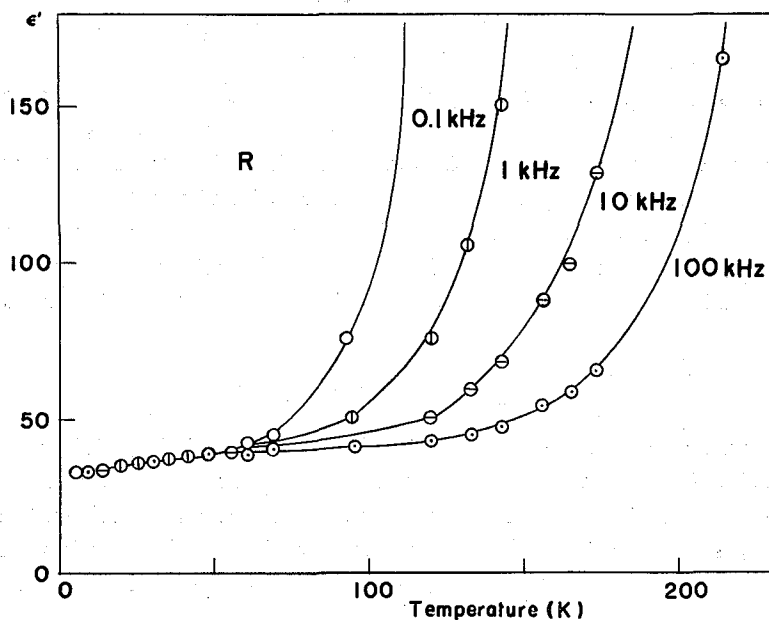


Fig. 1. Temperature dependence of dielectric constant of $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ (R) in the temperature range from 4.2 K to 200 K.

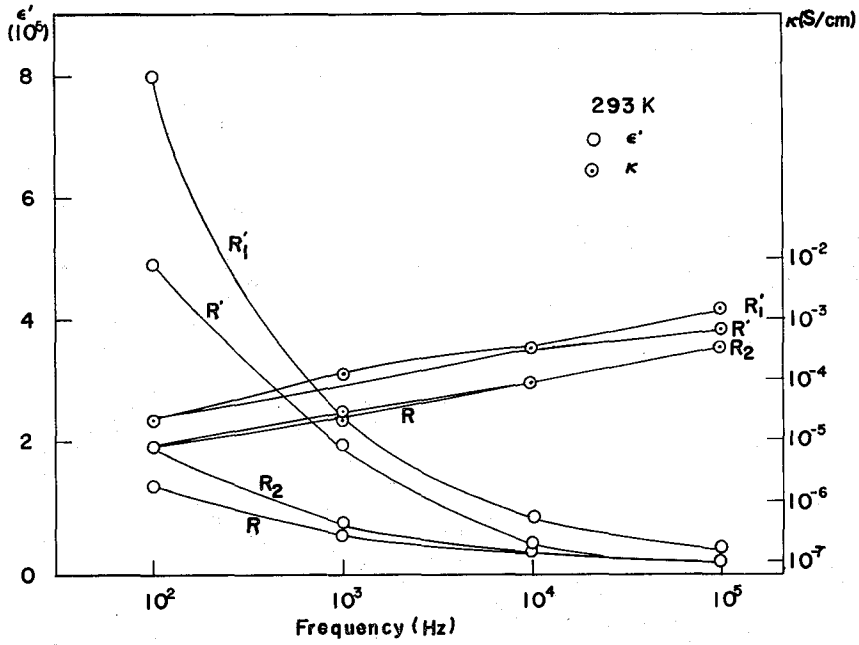


Fig. 2. Frequency dependence of dielectric constant and conductivity for the samples R, R1' and R2.

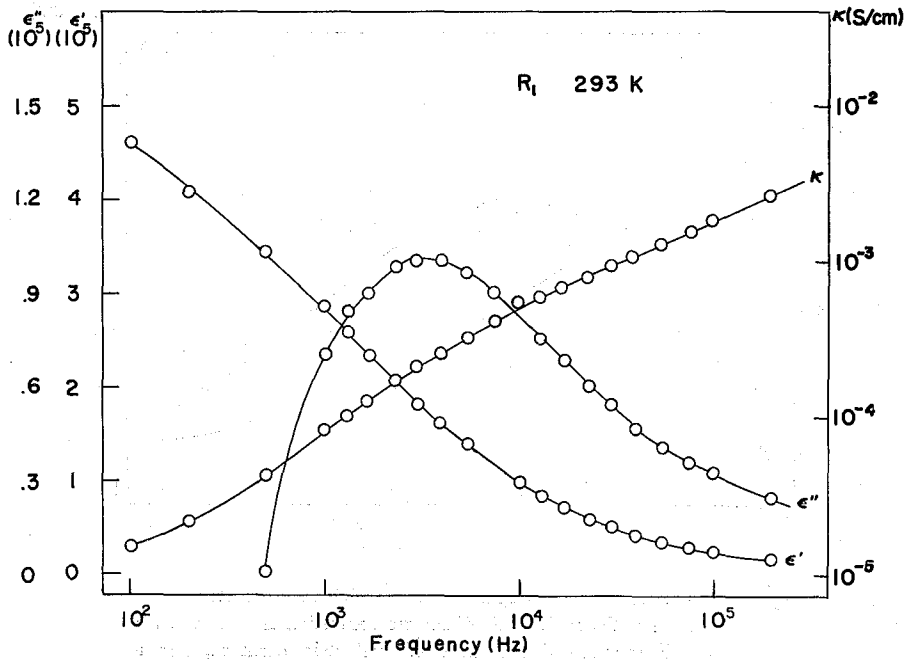


Fig. 3. Frequency dependence of dielectric constant, loss and conductivity of R1 at 293K.

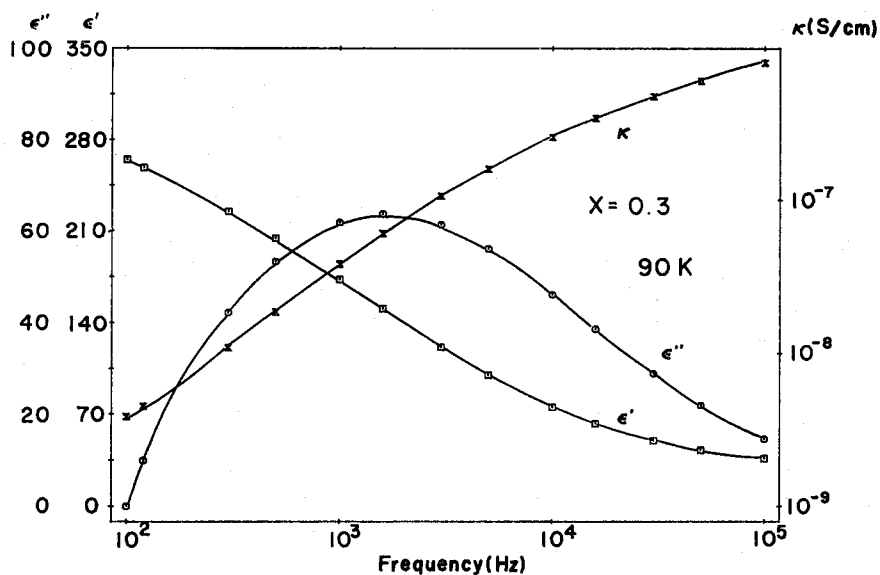
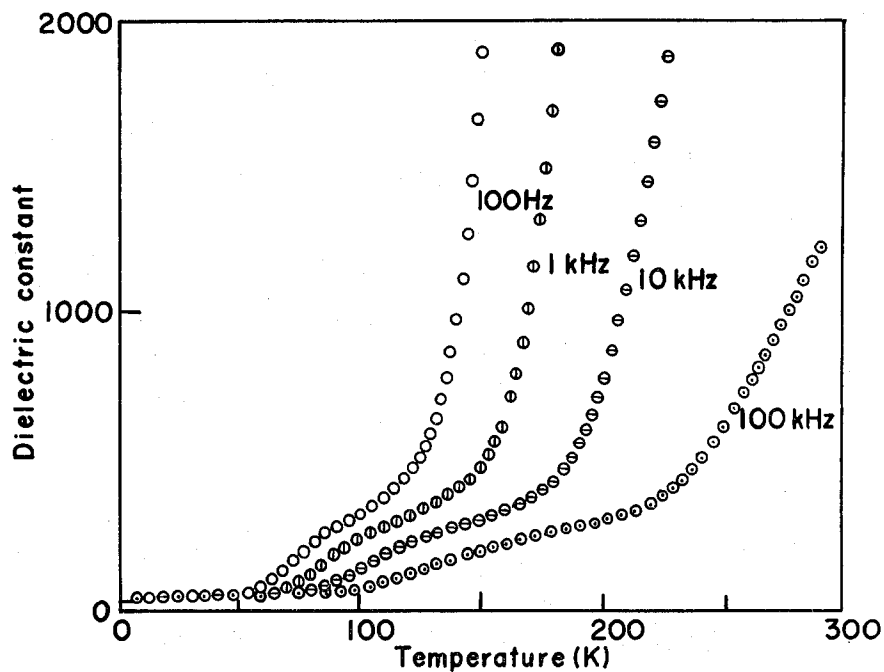


Fig. 4. (a) Temperature dependence of dielectric constant of the sample with $x=0.3$. A dielectric relaxation is seen at 90 K. (b) Frequency dependence of dielectric constant, loss and conductivity of the sample shown in (a) at 90 K.

Dielectric and Magnetic Relaxations in $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$

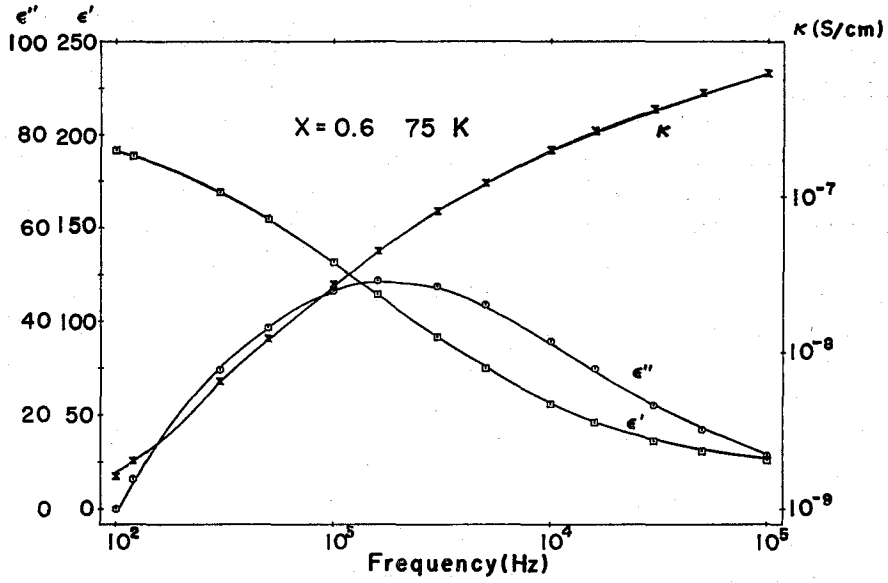


Fig. 5. Frequency dependence of dielectric constant, loss and conductivity of the sample with $x=0.6$ at 75 K .

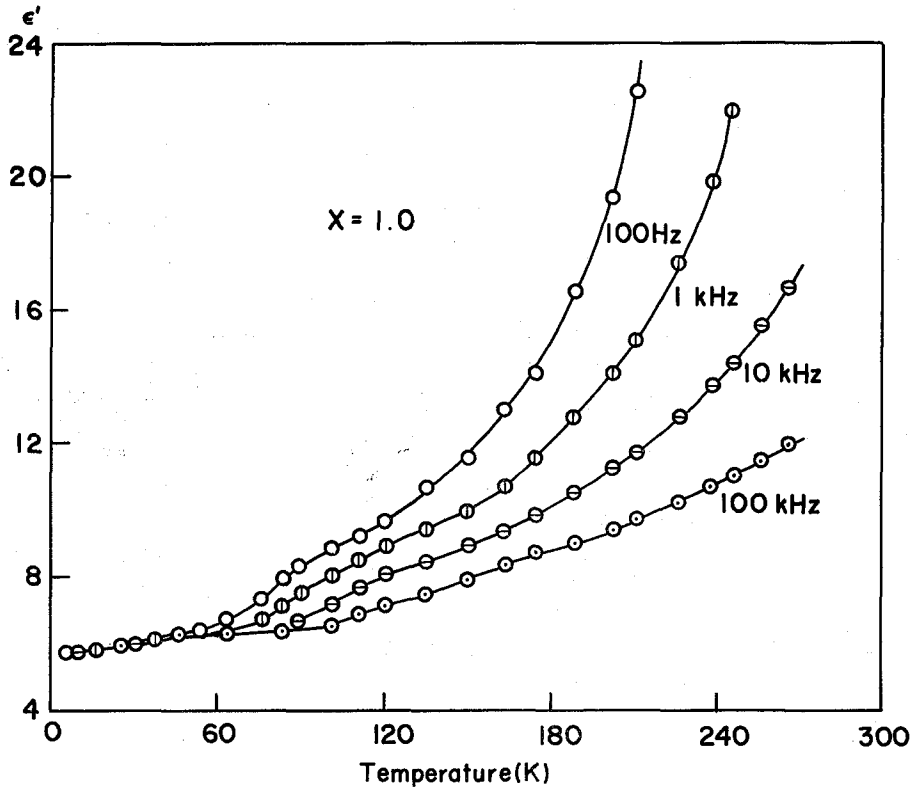


Fig. 6. Temperature dependence of dielectric constant of $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ ($x=1$).

was observed at lower frequencies for all the samples. Conductivities are in the range from 10^{-5} to 10^{-3} S/cm. The sample R1 exhibited dielectric dispersion with large relaxation intensity as shown in Fig. 3. This kind of dielectric relaxation was observed in some samples at room temperature, being noted as the **B** relaxation in Table III. The last column of Table III shows dielectric constant of the samples at 100 Hz which exhibit no **B** relaxation. All samples except $x=1$ have large dielectric constant at room temperature. The sample with $x=1$ has very low dielectric constant. Dielectric constant is large as far as a sample contains any amount of Ti ions. Titanium ions seem to make a sample conductive and increase dielectric constant.

In the sample with $x=0$ prepared in O_2 a dielectric relaxation was found at 31 K and dielectric constant increases rapidly with temperature and another dielectric relaxation of $\Delta\epsilon=3.1 \times 10^5$ appears around room temperature. For the sample with $x=0.3$ prepared in air only a dielectric relaxation with $\Delta\epsilon=8.45 \times 10^4$ was observed at 293 K, while the sample with $x=0.3$ prepared in O_2 exhibited two dielectric relaxations at 300 K with $\Delta\epsilon=5 \times 10^5$ and at 90 K as shown in Fig. 4. The sample with $x=0.3$ prepared in air has no **A** dielectric relaxation in Table III. The sample with $x=0.6$ prepared in O_2 had no **B** relaxation but had **A** dielectric relaxation at 75 K as shown in Fig. 5. The compound $BaO \cdot 2SnO_2 \cdot 2Fe_2O_3$ ($x=1$) prepared in oxygen exhibited the temperature dependence of dielectric constant as shown in Fig. 6 where two dielectric relaxations are seen at 35 and 120 K, though the relaxation intensities are very small. Since $BaO \cdot 2SnO_2 \cdot 2Fe_2O_3$ has very low conductivity compared with that of $BaO \cdot 2TiO_2 \cdot 2Fe_2O_3$, the dielectric relaxation due to the Maxwell-Wagner interfacial polarization which appears at room temperature in $BaO \cdot 2TiO_2 \cdot 2Fe_2O_3$ does not appear at these lower temperature for $BaO \cdot 2SnO_2 \cdot 2Fe_2O_3$, because the relaxation times of dielectric relaxation due to the Maxwell-Wagner interfacial polarization is proportional to the resistivity of sample. At these low temperatures there is little

Table III Relaxation intensity and temperature of **A** and **B** dielectric relaxations and dielectric constant at room temperature.

Sample	A relaxation		B relaxation		dielectric constant at room temperature $\epsilon_{R.T}$
	T_A/K	$\Delta\epsilon_A$	T_B/K	$\Delta\epsilon_B$	
Samples prepared in oxygen					
x=0.3	90	297.5	300	5×10^5	
x=0.6	75	214.8	-	-	5×10^5
x=1.0	35	0.4	-	-	4.4×10^2
	120	3.1			
x=0	31	6.5	290	3.1×10^5	
Samples prepared in air					
R	-	-	-	-	1.5×10^5
R1	-	-	293	4.7×10^5	
R2	-	-	-	-	2.0×10^5
x=0.3	-	-	293	8.45×10^4	

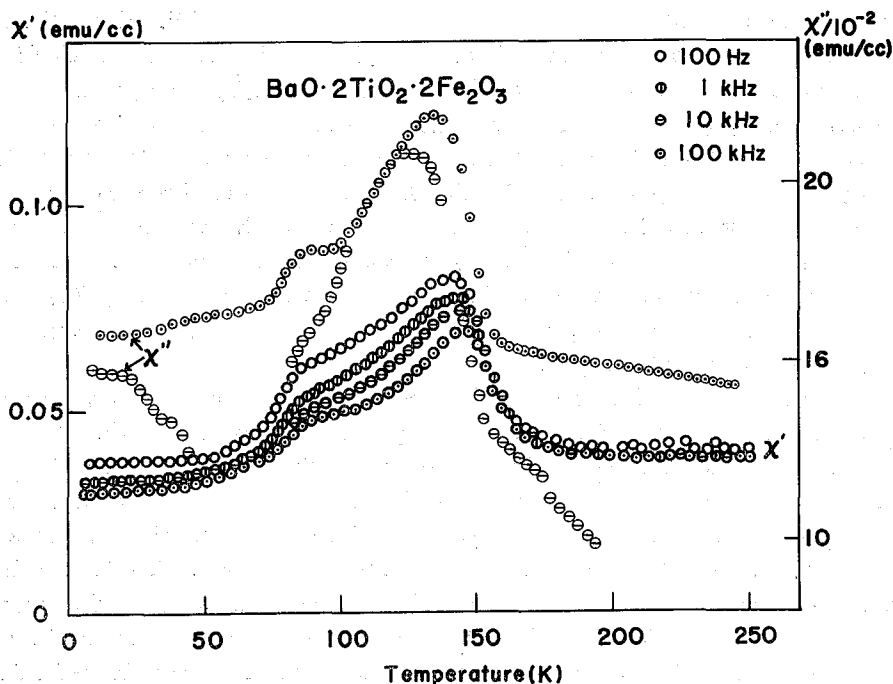


Fig. 7. Temperature dependence of magnetic susceptibility of R.

possibility of diffusion of atoms. Hence two electronic processes are expected for these relaxations with small relaxation intensity. The results of dielectric measurement are summarized in Table III. From this Table we find the A dielectric relaxation at low temperature appears only in the samples prepared in oxygen and not in the samples prepared in air. The sample prepared in oxygen may contain excess oxygen ions and cations with higher valency. Since the relaxation is seen in both $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ and $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ we suppose the origin of the relaxation is arising from Fe ions. Electron transfer between multivalent iron ions will bring about the dielectric relaxation. By the Onsager equation the concentration of higher valent ions is calculated to be 0.01, assuming that valence difference between cations is one and electrons hop between nearest neighbor cations. Two magnetic relaxations were observed in $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ as shown in Fig. 7. The magnetic relaxation at 165 K is different from the Debye type relaxation, while the magnetic relaxation at 80 K is the Debye type one. The cusp of real part of magnetic susceptibility with frequency dependence in χ' -T curve is usually found in spin glass materials. The peak of χ'' appears at the inflection point of χ' -T curve. This peak becomes small and appears at lower temperature with increasing x in the formula $\text{BaO} \cdot 2\text{Ti}_{1-x}\text{Sn}_x\text{O}_2 \cdot 2\text{Fe}_2\text{O}_3$. The sample with $x=0.3$ has only one peak of susceptibility at 80 K.

We observed the superposition of the cusp on the magnetic relaxation at 80 K. The magnetic relaxation at 80 K is related with the above mentioned mechanism of electron transfer. The relaxation at 165 K seems to be the spin glass transition. There are many reports which explain the spin glass transition by a blocking of superparamagnetic clusters^{5,6)}. It was reported that $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ has no long range magnetic

order and has superparamagnetic clusters with the size of 10^{-20} cm^3 ⁷⁾. Hence the origin of the spin glass transition in $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ may be due to the blocking of magnetic clusters. The lattice constant of $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ is larger than that of $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ as shown in Table II. As a result of large lattice constant of $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ the distance between Fe-Fe ions becomes larger for $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ and the exchange interaction between Fe-Fe atoms becomes very weak. Then the spin glass behavior found in $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ is not observed in $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$, while $\text{BaO} \cdot 2\text{SnO}_2 \cdot 2\text{Fe}_2\text{O}_3$ showed the ordered magnetic phase at 4.2 K by Mössbauer spectrum. However, there is a possibility that $\text{BaO} \cdot 2\text{TiO}_2 \cdot 2\text{Fe}_2\text{O}_3$ is a reentrant spin glass material, in which we observe two transitions: T_c (curie point) and T_g (spin glass transition point).

The **B** dielectric relaxation observed near room temperature is not always found for all samples. This was observed in both samples prepared in oxygen and air. From these properties we suppose that the **B** relaxation is due to the Maxwell-Wagner interfacial polarization arising from the heterogeneous structure of a sample. If we consider two phases **a** and **b** in a sample and assume $\epsilon_a = \epsilon_b$, we obtain conductivities: $\kappa_b = 5.5 \times 10^{-4} \text{ S/cm}$ and $\kappa_a = 2.2 \times 10^{-7} \text{ S/cm}$, the volume fraction of phase **a**: 0.01 and dielectric constants: $\epsilon_a = \epsilon_b = 2.2 \times 10^3$ for the sample with $x=0$ prepared in oxygen by using the Maxwell theory for stratified two layers⁸⁾. The phase **a** with low conductivity and volume fraction of 0.01 may correspond to the grain boundary of the sintered oxide.

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